Oxidation Catalysis

Feringa, Bernard

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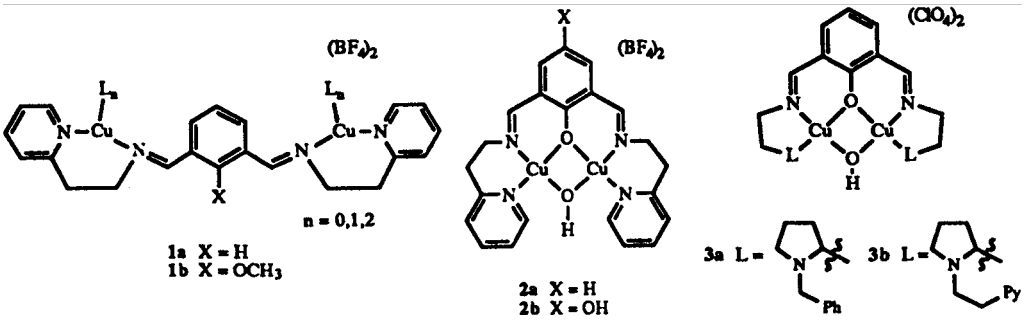
L09 OXIDATION CATALYSIS: A DINUCLEAR APPROACH

Ben. L. Feringa
Department of Organic Chemistry, University of Groningen, Groningen, The Netherlands

The binding and activation of molecular oxygen on polynuclear copper centers are essential features of various copper proteins such as the O_2-carrier hemocyanin and the monooxygenase tyrosinase. In biomimetic approach to new catalysts for stereoselective oxidations with O_2 achiral[1] and chiral non-racemic dinuclear copper(I) and copper(II) complexes **1-3** were prepared. The syntheses, molecular structures and reactivity in stoichiometric and catalytic oxidations with O_2 and oxygen-donors will be presented.



Arene hydroxylation, being a model system for monooxygenases, was observed for **1a** in the presence of O_2 whereas an intriguing hydroxylation-demethoxylation sequence was found for **1b**. A mechanistic study established dual oxidative pathways.

Using a pyridazine as a bridging unit between two Cu centers. O_2 activation is followed by hydroxylation α to the amine moiety in the ligand. We generated also hydroquinone Cu(II) complexes such as **2** and could demonstrate for the first time oxidative coupling and polymerisation reactions of phenols employing well-characterized dinuclear copper catalysts.

Modification of the chelating ligands in **2**, retaining the bridging 2,6-bisimino-phenol unit, resulted in novel dinuclear Cu(II) and Ni(II) complexes.[3] Both complexes with four and five coordinated metal centers are presented. Structural and electrochemical properties as well as results on catalytic epoxidations with various oxygen donors will be reported.

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